The role of sodium carbonate in PAM coagulation-flocculation for oil acidized wastewater treatment
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ABSTRACT
The pH value of oil acidized wastewater is relatively low (pH = 6.1), which seriously affects the flocculation of polyacrylamide (PAM). NaOH was used to adjust the pH value, but the maximum was only 7.5. The regulation was limited as the Ca2+ in aqueous phase up to 1,350 mg L⁻¹ consumed OH⁻. A novel formulation of Na₂CO₃ + PAM was proposed to form CaCO₃ floc core to facilitate PAM coagulation. When the concentration was above 400 mg L⁻¹, the PAM precipitation tended to be maximum, followed by NaOH adjustment of pH to 8.0 that could enhance PAM flocculation successively. The sewage sludge (SS) remained and residue oil reduced to 25 mg L⁻¹ and 34 mg L⁻¹ respectively. The analysis of the species and composition of fatty acids indicated that the coagulation-flocculation selectively effected the sedimentation of saturated fatty acids (SAT). This provides a new idea for recovery of high value-added residual oil. The optimal additive of Na₂CO₃ is expected as promising coagulant aid to improve the PAM coagulation-flocculation of oil acidized wastewater.

Key words | Ca²⁺, floc core, oil acidized wastewater, PAM

INTRODUCTION
The operation of acid fracturing, which is used to boost yield, is common in oil and gas wells, so oil extraction wastewater possesses high acidity and strong corrosion. As reported in literatures, the wastewater contains large amounts of calcium chloride up to 3 × 10³ to 2.8 × 10⁴ mg L⁻¹ (Wang et al. 2004). The Ca²⁺ in aqueous phase consumes OH⁻ resulting in difficulty in pH adjustment and water treatment. The conventional treatments so far are composed of flocculation, neutralization, oxidation and AC sorption (Wang et al. 2016). But the problem was still not settled perfectly on account of the wastewater characteristic of low pH. In this study, a new approach to increase the PAM flocculation during the Na₂CO₃ addition is investigated. The addition of Na₂CO₃ is not only as an alkaline additive to improve the pH of wastewater slightly, but also coagulates calcium ions to form insoluble calcium carbonate, the fine precipitates absorbing suspended solids effectively (Hassani et al. 2008).

A novel formulation of coagulation-flocculation process was anticipated in wastewater treatment (Hassani et al. 2008). Under the high pH conditions, the negative surfaces of calcium carbonate were modified by cationic PAM significantly and increased the adsorption of humic acid (Bob & Walker 2001). However, there has been a long time argument with the role of calcium carbonate in coagulation-flocculation. Apparently, the CaCO₃ can easily form a floc core. The precipitates acted by the sweep coagulation mechanism affecting the sewage sludge (SS) removal, separating from water to introduce precipitation of heavy metals, phenolic compounds and long chain fatty acids efficiently (Lee et al. 2007; Greenberg et al. 2005). The electrical
double layer (EDL) between colloid particles was compressed by the dissolved calcium ion, which made the colloid size bigger and forming flocs easier (Sudoh et al. 2015). When low lime is used in drinking water treatment, the calcium carbonate contributes to PAM coagulation and settlement (Leentvaar & Rebhun 1982). Conversely, the improper way of adding PAM will impede the precipitation of calcium carbonate. The higher concentration induced more convex and concave shapes presented on the surface of calcium carbonate crystals (Peronno et al. 2015).

The lower pH value of oil acidized wastewater weakens the effectiveness of PAM flocculation. To elucidate whether adding Na₂CO₃ assists the formation of CaCO₃ floc core and improves the PAM flocculation, the removal of SS and residue oil in supernatant were examined. Comparing the effects of adding PAM and Na₂CO₃-PAM, there is a new insight into the role of Na₂CO₃ in coagulation-flocculation. Moreover, the Na₂CO₃ possibly selectively recycles the high value-added residual oil from wastewater.

**MATERIALS AND METHODS**

**Materials**

In this investigation, wastewater was collected from Changqing Oil Recovery Station located in Inner Mongolia, which was stored at 4°C prior to use. The reagent of EDTA, calcium red indicator, methanol, n-hexane, methyl tert-butyl ether and petroleum ether were purchased from Sigma-Aldrich (MO, USA), respectively. A novel formulation of Na₂CO₃ coagulant (Merck, Germany) PAM flocculants (Cationic C-100, SNF Co., China) was used for SS and oil removal. All the reagents were of analytical reagent grade, and were dissolved in water purified with both a deionizing-distilling apparatus and a MilliQ apparatus (Millipore, USA). The solution pH was measured with a pH meter (TOA DKK, Japan). The concentration of calcium ions was determined by EDTA titration.

**Methods**

**Coagulation-flocculation experimental procedures**

Experiments were carried out in a jar-test apparatus, equipped with beakers of 500 mL volume. At the beginning, 200 ml of oil acidized wastewater was taken, coupled with pH adjustment, six strategies of NaOH-Na₂CO₃-PAM addition were adopted: in the absence of NaOH and PAM, Na₂CO₃ was added with concentrations of 0, 400, 800, 1,600 and 2,000 mg L⁻¹ (i.e. 0, 4, 8, 15 and 19 mmolL⁻¹) respectively, to obtain the CaCO₃ coagulants. Since the oily wastewater had high polymer residue, 200 mg L⁻¹ PAM was used as flocculant, the dosage selection being based on practical application in the oil field (Zhao et al. 2008). Apart from PAM, 0, 30, 60, 120 and 150 mg L⁻¹ NaOH was blended with wastewater in the control. Instead of NaOH, 0, 400, 800, 1,600 and 2,000 mg L⁻¹ Na₂CO₃ were added respectively for each coagulation-flocculation experiments. In the case of NaOH at 120 mg L⁻¹, the experiment was carried out by addition of 0, 400, 800, 1,600 and 2,000 mg L⁻¹ Na₂CO₃ separately. Last, when the Na₂CO₃ was maintained at 800 mg L⁻¹, the experiment was conducted by adding NaOH at 0, 30, 60, 120 and 150 mg L⁻¹ respectively.

After rapidly mixing for 10 s at 150 rpm and slowly mixing for 1 min at 30 rpm, the liquid was clarified for 10 mins (Amuda & Amoo 2007). 50 ml of supernatant was taken for SS (in mg L⁻¹) gravimetric determination, 40 ml of supernatant was taken for oil content UV analysis, 100 μl of flocculate was picked out and diluted with MilliQ water to observe the precipitate by 40× microscope (BX61, Olympus, Japan). Unless otherwise stated, all experiments were performed in triplicate and sampled after 10 mins.

**The analysis of oil content**

The 40 ml of supernatant from coagulation-flocculation was blended with 10 ml of petroleum ether in 50 ml of centrifuge tube. Sample extraction was conducted with a reciprocate shaker (incubator personal Lt, TAI TEC, Japan) for 2 h; afterwards, the mixture was centrifuged at 10,000 rpm for 10 mins to break the emulsion. The supernatant was withdrawn to measure the UV absorbance (UV 2450 PC, Shimadzu, Japan) at 235 nm (Mao & Han 2013).

**The analysis of fatty acid**

After saponification and methylation of 0.5 g precipitate, 1 ml of premixed solvent (n-hexane: methyl tert-butyl ether = 1: 1) was added for extraction, and the upper organic phase was taken for the GC-MS analysis.
RESULTS AND DISCUSSION

The formulations of NaOH and Na$_2$CO$_3$ effects on the pH value and Ca$^{2+}$ removal

As shown in Figure 1(a), with the increased concentration of NaOH, the pH value of the wastewater rose to 7.9. A plateau was observed at high equilibrium concentrations, suggesting the limited capacity of NaOH to adjust pH. Meanwhile, the discrepancy of pH regulated by NaOH between 1 and 10 mins implied that a weak acid buffer system may consume OH$^-$ as time increases. The original calcium in wastewater was up to 1350 mg L$^{-1}$ based on the titration of EDTA in the solution. Addition of NaOH from 0.75 mmol to 3.75 mmol resulted in the consumption of Ca$^{2+}$ from 0.4 mmol to 2 mmol, which demonstrated the consumption ratio of OH$^-$:Ca$^{2+}$$\approx$ 2:1. The Ca$^{2+}$ in the oil wastewater neutralized most of the OH$^-$ to form Ca(OH)$_2$. Although 30 mg L$^{-1}$ NaOH theoretically provided $7.5 \times 10^{-4}$ mol L$^{-1}$ OH$^-$, only $6 \times 10^{-7}$ mol L$^{-1}$, 0.8 % OH$^-$ was used to adjust the pH value within 1 min. Similarly, there were $4 \times 10^{-7}$ mol L$^{-1}$ and 0.5 % OH$^-$ for the regulation of pH within 10 mins. It is demonstrated that Ca$^{2+}$ and H$^+$ compete to bind with OH$^-$ and there is greater reactivity of Ca$^{2+}$ than the reaction of H$^+$.

Figure 1(b) presents the effect of sodium carbonate on the pH value of oil acidized wastewater. The consumption of Na$_2$CO$_3$ and Ca$^{2+}$ was 1:1. As the content of Na$_2$CO$_3$ increased more than 15 mol L$^{-1}$, the pH value of the solution reached 7.4. Na$_2$CO$_3$ was inherently a weak alkaline reagent; the dissolved CO$_3^{2-}$ in the wastewater was rapidly captured by Ca$^{2+}$ to form precipitated nuclei, and the rest of the Na$_2$CO$_3$ reacted with H$^+$ in liquid to present a partial capability for pH adjustment. As shown in Figure 1(a), 4 mol L$^{-1}$ Na$_2$CO$_3$ cooperated with 0.75 mol L$^{-1}$ NaOH significantly increased the aqueous pH to 8. Here, the ratio of CO$_3^{2-}$:Ca$^{2+}$$= 1:1$ and the CaCO$_3$ coagulation was preferentially formed, the reaction of CO$_3^{2-}$ to Ca$^{2+}$ was stronger than that between OH$^-$ and Ca$^{2+}$. Conversely, 1 % OH$^-$ was used to regulate the pH value and the utilization of NaOH was tripled.

The effect of precipitated CaCO$_3$ on the coagulation and flocculation

It can be seen from Figure 2(a) that the PAM produced floc is a loose group and light grey. The lower adsorption of PAM contributed to the acidic pH of 6. Either the pollutant was in a highly ionized state, where the surface was close to the point of zero charge, or the expanded form of the PAM

Figure 1 | The effect of NaOH (a) and Na$_2$CO$_3$ (b) on the pH value (solid line) and Ca$^{2+}$ (dashed line) depletion of oil acidized wastewater.
polymer coil, which covered more surface area on adsorption (Besra et al. 2004). Additionally, in Figure 2(b), when the pH adjustment was done by NaOH, the number of clusters increased, and the PAM floc became bigger and the settling speed was accelerated. The colloidal particles from long distance came through the bridge to form loose flocs with much internal water (Wu et al. 2000). But this looser structure was susceptible to the exterior environment and easily broken up (Jarvis et al. 2005).

Figure 2(c) shows the prominent coagulation of Na₂CO₃ in the wastewater. The CO₃²⁻ is preferentially bound with calcium ions and produces a CaCO₃ floc core ($\phi = 1–2 \, \mu m$). The coagulated nuclei adsorb contaminants from the wastewater to form fine pellet precipitates and shorten the settling time (Sudoh et al. 2015). At a neutral pH of 7.4, CaCO₃ particles were neutral or slightly positively charged. Thus, a high adsorption affinity of the negatively charged pollutant was observed. In Figure 2(d), PAM as bridge and CaCO₃ as coagulant aid were applied to the wastewater. The flocs coiled around the CaCO₃ were supposed to increase the volume and weight of the settling sludge, showing a dark black core. The CaCO₃ as the porous adsorbent (Sudoh et al. 2015) improved the cohesive force and made a faster liquid-solid separation, consequently it was no longer vulnerable under the action of hydrodynamic shear force (Gray & Ritchie 2006). Comparing the results of Figure 2(d) to Figure 2(a)–2(c), CaCO₃ as the coagulant aid and nuclei was wrapped with coiled floc, which made the biggest clusters, easier settled and harder to break up. As a consequence, the supernatant was clearer and the handling result was more stable.

The effect of sole Na₂CO₃ on coagulation-flocculation

As shown in Figure 3(a), with the increase in time, the removal of SS and residue oil were improved. The maximal clarifications were 37% and 84% respectively. Comparing the processing effect between 40 and 10 mins, the removal of SS was increased by 19% for 40 mins, while the difference in oil removal was negligible.

Figure 3(b) experiments show that the high concentration of Na₂CO₃ increased the flocculation and raised the corresponding pH value. As the concentration was 400 mg L⁻¹, Na₂CO₃ adjusted the pH value to 6, and the removal efficiency of SS was up to 22%. As the
concentration was 800 mg L\(^{-1}\), the adjustment of pH value was up to 7, the removal of residue oil attained the maximum of 68%. A plateau was observed at high equilibrium concentrations, suggesting monolayer coverage on the calcium carbonate surface (Bob & Walker 2001). The isoelectric point (IEP) for CaCO\(_3\) particles was around pH 8.1 (Thompson & Pownall 1989). When the pH of the solution equaled 6 or 7, the calcium carbonate particles were positively charged or uncharged, and obtained highly adsorptive affinity to the negatively charged pollutant. It can be seen that the increase of the processing time and the amount of sodium carbonate can promote the precipitation, so as to further purify the water quality.

**Figure 3** | The effect of settling time (a) at 800 mg L\(^{-1}\) Na\(_2\)CO\(_3\) and varying Na\(_2\)CO\(_3\) concentrations (b) on the removal of SS (square) and residue oil (circle).

The effect of NaOH on the coagulation-floculation of Na\(_2\)CO\(_3\)-PAM

The result of Figure 4 demonstrates the influence of NaOH on removal of SS and residue oil solely by PAM and combined Na\(_2\)CO\(_3\)-PAM respectively. In the absence of NaOH, the SS residue after adsorption of PAM was 293 mg g\(^{-1}\). In contrast, an equivalent of PAM and 800 mg L\(^{-1}\) of Na\(_2\)CO\(_3\) were used to remove SS, and SS residue declined to 256 mg g\(^{-1}\).

The adjustment of pH done by NaOH influenced the PAM flocculation and affected the PAM molecular chain stretch (Besra et al. 2004). The higher pH gave rise to higher efficiency flocculation. When the concentration of
NaOH approached 60 mg L\(^{-1}\), the PAM flocculation attained its maximum. The SS residue was lowest at 217 mg L\(^{-1}\) and the removal ratio of oil was highest at 88%. However, a plateau was observed at high equilibrium concentrations of NaOH, suggesting pH in a certain range can promote PAM flocculation.

As can be seen, the removal of residue oil and SS by PAM-CaCO\(_3\) was better than the sole function of PAM. Specifically, when the Na\(_2\)CO\(_3\) and NaOH were added at 400 mg L\(^{-1}\) and 120 mg L\(^{-1}\) respectively, the SS declined to 10 mg L\(^{-1}\) and 97% of the removal ratio, while the reduction of residue oil was around 85%. This was consistent with the values in the literature (Bob & Walker 2001); cationic polyacrylamide cooperated with calcium carbonate particles to promote the adsorption, and so on to increase of the flocculation effect. However, the removal was influenced both by electrostatic interactions and chemical interactions between contaminant particles and PAM-CaCO\(_3\). Petrovic et al. pointed out that the ligand exchange played a role in adsorption of calcium (Petrović et al. 1999). In this work, the experimental environment was carried out at pH about 7.5, the net electrophoretic mobility of PAM-CaCO\(_3\) particles was positive (Bob & Walker 2001), and facilitated the attachment of SS and oil to PAM-CaCO\(_3\). However, it cannot interpret an increasing removal of SS and oil corresponding with the increase in NaOH. We assumed that the higher pH had a more significant effect on the negative charge of the contaminant colloidal, which resulted in the higher amount of adsorption by PAM-CaCO\(_3\).

The effect of Na\(_2\)CO\(_3\) on the PAM coagulation

As Na\(_2\)CO\(_3\) increased, the pH value rose to 7.4 and 7.7 in the absence and presence of 120 mg L\(^{-1}\) NaOH respectively (shown in Figure 1(a)). A steady stream of porous CaCO\(_3\) was generated to attach more contaminants (Sudoh et al. 2015). Figure 5 demonstrates the performance of coagulation-flocculation as a function of Na\(_2\)CO\(_3\). Calcium ions were homogeneously blended with SS and residue oil beforehand in wastewater, which blocked the negatively colloidal particles and acted as bridges between functional groups of the two adjacent molecules (Duan et al. 2005). CaCO\(_3\), acting as a coagulant aid by forming larger flocs, shortened the settling time for the removal of DOC (Sudoh et al. 2015). The removal efficiency of SS and residue oil by adding Na\(_2\)CO\(_3\) and PAM simultaneously was better.
than successively (Figure S1, available with the online version of this paper), which once again proved that the CaCO₃ as condensed nuclei coagulated with PAM flocs facilitated the coagulation-floculation.

In the presence of NaOH at 120 mg L⁻¹, the PAM floculation enhanced the increase of Na₂CO₃ to 2,000 mg L⁻¹, the removal of residue oil approached the maximum of 90% and the residue SS declined to the minimum of 25 mg L⁻¹. The dissolved Ca²⁺, compressing the EDL between colloids at higher pH, made SS and residue oil cohesive and easy to sink (Iakovides et al. 2019). Consequently, the effect of coagulation-floculation was cumulatively enhanced by adding NaOH to the Na₂CO₃-PAM system.

**Effects of Na₂CO₃ on selective deposition of fatty acids for oil recovery**

Only a few reports so far have focused on the species of fatty acids in oil-containing wastewater. A complex mixture of alkyl-substituted acyclic and cycloaliphatic carboxylic acids in wastewater is named naphthenic acids (NAs). NAs can be divided into saturated fatty acids (SAT) and unsaturated fatty acids (UFA). Acyclic carboxylic acid as the major part of naphthenic acid in the Changqing oil accounted for 48.08%, followed by cycloaliphatic carboxylic acids at 34.11%, the low content of phenylalkanoic acid was 17.79% (Liu et al. 2018). SAT contained more energy than UFA, and thus the ubiquitous NAs in oil wastewater required to be removed and recovered efficiently. In raw oil acidized wastewater (Figure 6), the fatty acids were mainly composed of SAT and mono-UFA, accounting for 95% and 5% respectively, but the content of polyunsaturated fatty acids was small and negligible.

As shown in Figure 6, adding Na₂CO₃ to the oil wastewater, the UFA content decreased from 65% to 35% with the increase of Na₂CO₃. Most of the UFA entered the supernatant, indicating that CaCO₃ was selectively combined with SAT in wastewater. The selective sedimentation of SAT was conducive to the recovery of residue oil. Similarly, a significant loss of C20:5 was detected in sludge when the fatty acid was separated by floculation. Borges et al. also found that addition of PAM led to high levels of C14:0 and low content of C20:5 trapped by the floculants (Borges et al. 2011). The positive part of the floculant adhered to the fatty acid and the negative formed bridges with medium components, causing the UFA crawling to

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**Figure 5** | Effect of PAM cooperated with 0 mg L⁻¹ and 120 mg L⁻¹ of NaOH on the removal of SS (histogram) and residue oil (linear) as a function of Na₂CO₃.
the culture medium. Thus, the difference in the percentage of fatty acids may be due to the remaining UFA in the supernatant, not the entry into sedimentation during the flocculation (Martínez et al. 2014).

Compared with the distribution of fatty acids in the original wastewater, the percentage of UFA in the supernatant gave rise to 15% solely by PAM flocculation. This rose to 54% in the presence of Na₂CO₃ + PAM, indicating that both PAM and Na₂CO₃ had a selective sedimentation on SAT. Na₂CO₃ and PAM interacted with each other to promote the coagulation-flocculation, both together had a stronger settling effect on the species of fatty acids. The equivalent PAM along with different concentrations of NaOH was used in Figure 6, the ratio of SAT/UFA basically remaining at 1.3. The ambiguous effect was possibly due to the excessive calcium ions disabling the impact of NaOH on pH value. However, at the addition of 800 mg L⁻¹ Na₂CO₃, the ratio of SAT/UFA decreased gradually with the increase in NaOH; the equilibrium state was at 0.5. The residual concentration of SAT being 14 mg L⁻¹ in the

![Figure 6](https://iwaponline.com/wst/article-pdf/77/11/2677/244559/wst077112677.pdf)

**Figure 6** | Effect of PAM (grey histogram), Na₂CO₃ + PAM (white histogram), NaOH + PAM (square) and 800 mg L⁻¹ Na₂CO₃ + NaOH + PAM (circle) on the removal of SAT (grids) and UFA (diagonal) in oil acidized wastewater (a), and the removal ratio related to the varieties of SAT/UFA which derived from experimental data of Na₂CO₃ + PAM, NaOH + PAM and 800 mg L⁻¹ Na₂CO₃ + NaOH + PAM (b).
The supernatant confirmed that CaCO₃ precipitates promoted the selective sedimentation of fatty acid species. In high pH-induced flocculation-sedimentation researches in the productivity of bio-diesel, therein more Na₂CO₃ than SAT were found, the increase of fatty acid unsaturation might be a mechanism of adaption to environmental conditions (Castrillo et al. 2013). Although an increase of UFA was detected in supernatant at pH values below 8, the reason for this was unclear. Consequently, the association of removal ratio to the SAT/UFA was investigated in Figure 6(b). As can be seen, the relationship is presented as y = 86.4x – 3.72 with correlation coefficient R² of 0.8, the selective deposition of NaOH was considered to follow a uniform mechanism. Based on the tendency line, we suspected that the distribution of fatty acids is highly related to the degree of removal ratio in coagulation-flocculation.

CONCLUSIONS

The data presented in this research propose one way to improve the PAM flocculation of SS and residue oil by the addition of Na₂CO₃. Oil acidized wastewater obtained a pH value at 6.1, herein the calcium ion was up to 1,350 mg L⁻¹ and consumed NaOH at 99%. The released CO₃²⁻ binding with Ca²⁺ faster than OH⁻ suggested that Na₂CO₃ + NaOH enhanced the utilization of OH⁻ to neutralize. In the presence of pH 6.1–7.5, CaCO₃ particles expressed positive charges under the IEP of 8.1, the electrostatic attraction was primarily at the interface of particles and contaminants, facilitating the SS and residue oil to attach to PAM-CaCO₃. The increase of NaOH was beneficial to PAM flocculation because of the stretch of the PAM molecular chain. Under the premise of Ca²⁺ homogeneously blending with contaminants, the Na₂CO₃ collected Ca²⁺ together to generate a CaCO₃ floc core, as a coagulant aid to improve coagulation-flocculation. Besides, the CaCO₃ and PAM selectively combined with SAT to settle down in favor of high-value oil recovery. The optimal formulation was suggested as 200 mg L⁻¹ PAM, 120 mg L⁻¹ NaOH and 400 mg L⁻¹ Na₂CO₃. In this case, the content of SS and oil was reduced to 25 mg L⁻¹ and 34 mg L⁻¹ respectively, which almost met the requirements of MCLs and maximized the recycling of SAT. A novel hybrid technology combing with Na₂CO₃ coagulation and PAM flocculation is highly recommended to effectively remove contaminants in oil acidized wastewater. Future work is needed to explore the size effect of precipitated CaCO₃ on coagulation-flocculation. In addition, this study could expand to other different coagulants as the floc core to decontaminate in acidized environments.

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